



A highly active nano-micro hybrid derived from Cu-bridged TiO₂/porphyrin for enhanced photocatalytic hydrogen production

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ABSTRACT

Development of photocatalysts with high activity and durability for hydrogen generation is extremely desired but still remains a great challenge currently. With Cu nanoparticles (Cu NPs) as a linker between TiO₂ microsphere (TiO₂ MS) and 5, 10, 15, 20-*meso*-tetra(4-carboxyphenyl)porphyrin (TCPP), a novel nano-micro hybrid (TiO₂ MS-Cu-TCPP) was prepared via a facile method. By bridging TiO₂ MS and TCPP with Cu NPs, the absorption and the electron transfer of TiO₂ MS were greatly improved. When the TiO₂ MS-Cu-TCPP was employed as the photocatalyst for hydrogen evolution, it exhibited higher activity and stability than those of the TiO₂ MS, the TiO₂ MS-Cu and the TiO₂ MS-TCPP, TiO₂ MS-Cu-CuTCPP and TiO₂ MS-TCPP-Cu. The photocatalytic activity was enhanced for about 6 times with respect to that of the pristine TiO₂ MS. The excellent performance for the nano-micro hybrid can be attributed to wide light absorption, more reactive sites, and facilitated interfacial electron transfer owing to the strong interaction between TiO₂ and TCPP with Cu NPs as the linker and cocatalyst. Subsequently, a high and stable photocatalytic activity over the TiO₂ MS-Cu-TCPP nano-micro hybrid was achieved, demonstrating the importance of interfacial modification to a semiconductor photocatalyst. This result gives us a new perspective of constructing special structures for efficient light utilization and electron transfer.

1. Introduction

Photocatalytic hydrogen production driven by free and sustainable solar energy is considered as one of the promising strategies for resolving global energy and environmental problems, owing to its production with no reliance on fossil fuels and no carbon dioxide emission [1–3]. As a promising candidate photocatalyst, TiO₂ is used widely because of its low cost, nontoxicity, availability, and stability against the light irradiation [4,5]. It is known that the photocatalytic performance of TiO₂ has close relationship with its morphology [6]. TiO₂ microsphere (TiO₂ MS) with three-dimensional mesoporous architecture can enhance light-scattering and light-harvesting, which shows excellent performance in photoelectric application [7]. Unfortunately, with pure TiO₂ as the photocatalyst, low visible adsorption due to its wide band gap, and quick electron-hole recombination extremely limit its photocatalytic performance for hydrogen evolution. Therefore, how to enhance its photocatalytic activity is still a significant issue. As frequently reported, the structural design of a photocatalyst plays a key role in determining the photocatalytic performance for hydrogen production, which requires high light absorption, fast electron transfer, and good stability [8,9]. Many approaches have been proposed, and

much effort has also been made to develop the novel photocatalysts with special structure to satisfy these requirements.

With high visible light absorption and straightforward solar energy-to-chemical conversion facility, porphyrins are regarded as excellent photoactive materials [10,11]. Sharon et al. reported that a visible photoactive porphyrin/TiO₂ composite prepared via adsorption at room temperature exhibits a good photocatalytic degradation activity for pharmaceuticals [12]. Georgios et al. reported a photocatalytic system with Sn-porphyrin as the photosensitizer, and the target complex exhibited high photocatalytic activity [13]. In these systems, the introduction of porphyrins can only enhance the light absorption of the photocatalysts, and the separation and transfer of photo-generated charges has been hardly affected.

Generally, fast charge carrier recombination for TiO₂ can be effectively inhibited by loading noble metal (Au, Ag, and Pt) [14]. Alternatively, loading with transition metals such as Cu, Fe, Co, and Ni has recently turned out to be a cheaper and efficient option [15]. Several reports have also revealed the effectiveness of Cu cocatalyst in photocatalysis over noble metals [16]. Therefore, by constructing the specific structure with Cu and porphyrin, it will be very advantageous for improving the activity of TiO₂-based photocatalysts. In our previous

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reports [17,18], it was found that the composites with high light absorption and electron transfer can be achieved by linking porphyrins onto the Cu_2O by means of hydrogen bond interaction and coordination interaction, which are very advantageous to improve the photocatalytic activity of Cu_2O . However, the problems, especially the difficult recovery due to its small size and the instability in strong acid/base, need to be solved. Therefore, it is still a challenge to construct special structures for stable, easily recovered, and highly efficient photocatalytic hydrogen production without loading additional cocatalyst. TiO_2 MS with three-dimensional mesoporous architecture is more stable in acidic or basic environment, and is easier to be recovered due to its larger size, which are important factors in catalysis research as well as for practical application.

Herein, a novel TiO_2 microsphere/meso-tetra(4-carboxyphenyl) porphyrin (TCPP) nano-micro hybrid linked by metallic Cu is facilely prepared by means of coordination interaction and electrostatic interaction. The as-prepared TiO_2 MS hybrid possesses unique hierarchical structure. The assembly mechanism of the hybrid is explored. Moreover, photocatalytic hydrogen production over the hybrid is investigated in detail. Fluorescence, photoelectronic response and electrochemical impedance are performed to elucidate the detailed mechanism of electron transfer.

2. Experimental

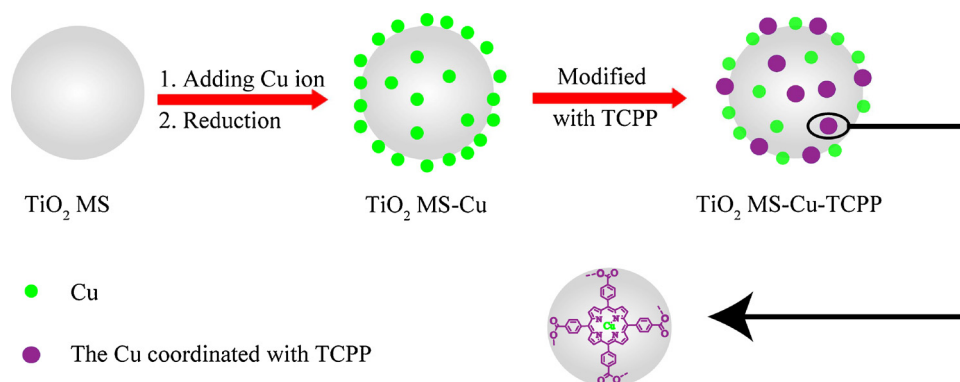
2.1. Materials

Polyethylene glycol 200 (PEG 200) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Company. Hydrazine hydrate, urea and ethanol were purchased from Shanghai Taitan Scientific Co., Ltd. TiCl_3 hydrochloric acid solution was purchased from Aladdin Industrial Co. Trisodium citrate dehydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) was purchased from Shanghai Chemical Reagent Company. Meso-tetra (4-carboxyphenyl) porphyrin (TCPP) was purchased from J&K Scientific Ltd. All chemicals used were analytical grade reagents without further purification.

2.2. Synthesis of the TiO_2 MS-Cu-TCPP hybrid

Firstly, TiO_2 MS were synthesized via a modified solvothermal process [19]. In a typical experimental procedure, 12 mL PEG 200 and 2.4 g urea were dissolved in 30 mL ethanol, and the solution was further magnetically stirred until it became clarified. Then, 12 mL TiCl_3 hydrochloric acid solution was added, and the mixed solution was transferred to a 100 mL Teflon-lined autoclave immediately. The autoclave was sealed and maintained at 150°C for 12 h. The solid was collected and washed with ethanol and distilled water, respectively, and dried at 60°C .

TiO_2 MS-Cu-TCPP hybrid was obtained by the following procedure



Scheme 1. Schematic illustration for preparing the TiO_2 MS-Cu-TCPP hybrid.

(Scheme 1).

In a typical synthesis, 120 mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added into 150 mL water, and then 300 mg TiO_2 MS was added. After being stirred for 40 min, 50 mL of 1.47 mol L^{-1} sodium citrate solution was added into the mixture, and continuously stirred until the color of the solution did not change any more. Then, 10 mL of hydrazine hydrate was added and slightly stirred overnight. Finally, the precipitate (TiO_2 MS-Cu) was collected by centrifugation, and washed and dried at 60°C .

100 mg of TiO_2 MS-Cu was added into 50 mL of $7.6 \times 10^{-6} \text{ mol L}^{-1}$ TCPP methanol solution, and stirred for 8 h at room temperature. The solid was collected, and dried in a vacuum oven at 60°C . Subsequently, TiO_2 MS-Cu-TCPP nanohybrid was obtained by hydrogen bond interaction coming from carboxylic groups of TCPP with the hydroxyl groups on TiO_2 MS (confirmed by the followed UV-vis spectra and FTIR spectra), and coordination interaction between the Cu on the TiO_2 MS and the N atoms located at the center of the TCPP macrocycle (evidenced by the followed UV-vis spectra, FTIR spectra and XPS spectra), just like that shown in Scheme 1. The content of TCPP in the hybrid was about 0.25 wt. %. For comparison, TiO_2 MS-TCPP, TiO_2 MS-TCPP-Cu and TiO_2 MS-Cu-CuTCPP were also synthesized by similar procedure.

2.3. Characterizations

Powder XRD diffraction was carried out using a Bruker D8 Advance X-ray diffractometer (Germany). The transmission electron microscope images were taken using a JEOL JEM-1400 microscope (Japan). The element maps were taken with a Hitachi S-4800 cold field emission scanning electron microscope operated at an accelerating voltage of 20 kV (Japan). The surface morphology of the samples was observed by S-3400 N Hitachi High Technologies scanning electronic microscopy (SEM, Japan). UV-vis absorption spectra were recorded with a UV-3900 spectrophotometer (Japan). Fourier transform infrared spectra (FTIR) were measured using a Nicolet 6700 FTIR spectrometer (USA). X-ray photoelectron spectroscopy analyses were performed using a Thermo ESCALAB 250X-RAY photoelectron spectrometer with an Al ($\text{K}\alpha$) X-ray resources (USA).

2.4. Photoelectrochemical measurements

The photoelectrochemical performance of all samples was measured by a CHI660E electrochemical system using a three-electrode cell (Shanghai Chenhua Instruments, China). An Ag/AgCl electrode was used as the reference electrode, a platinum wire as the counter electrode, and fluorine-tin oxide (FTO) glasses coated with the sample were utilized as working electrodes. Before being coated the sample, the FTO glasses were ultrasonically cleaned with double distilled water, acetone, chloroform and ethanol for 20 min, respectively, and then dried in the atmosphere. The working electrode was prepared via dip-coating and subsequently natural drying. In brief, 2 mg of sample was dispersed into

4 mL of water. After that, the mixture was dip-coated onto the FTO glass ($1 \times 1.5 \text{ cm}^2$), and then was dried in the atmosphere. A 150 W Xenon lamp was used as the light source. The distance between the lamp and the FTO electrode was 7 cm. The electrolyte solution was 0.5 mol L^{-1} of Na_2SO_4 aqueous solution, and bias voltage was set in 0.1 V. All measurements were carried out at room temperature.

2.5. Measurement of photocatalytic hydrogen evolution

The photocatalytic activity for hydrogen evolution over the samples was performed through a CEL-SP2 N water splitting system (Zhongjiao Jinyuan Instruments, China). For photocatalytic hydrogen evolution, 10 mg of photocatalyst was dispersed by a magnetic stirrer in an up-irradiated photocatalytic reactor containing an aqueous solution of triethanolamine (TEOA) (60 mL, volume ratio of water to TEOA is 5: 1). The reaction cell was connected to a gas circulation system, and the hydrogen evolved was analyzed by an online gas chromatograph (NaX zeolite column, high-purity N_2 as carrier gas, thermal conductivity detector). The reaction temperature was kept at about 5.5°C by a circulating water jacket. A 300 W Xe lamp was used as the light source. The gas produced was automatically sampled and analyzed by an online gas chromatography. Before the photocatalytic reaction, the reactor was evacuated by a vacuum pump and flushed by nitrogen for several times to ensure complete removal of oxygen.

3. Results and discussion

3.1. Material characterization

The TiO_2 MS-Cu-TCPP nano-micro hybrid was fabricated by means of hydrogen bond interaction and electrostatic interaction with Cu NPs as the linker. Scheme 1 shows the schematic illustration of the formation of the TiO_2 MS-Cu-TCPP hybrid. First, the TiO_2 MS was loaded with Cu NPs by electrostatic interaction and in-situ reduction, and then the TiO_2 MS-Cu was added into the TCPP solution. After reacted at room temperature, the TiO_2 MS-Cu-TCPP nano-micro hybrid was obtained, and showed relatively rough surface morphology (Fig. 1). The TiO_2 MS-Cu-TCPP hybrid was formed owing to the special interaction among TiO_2 , Cu NPs and TCPP, which will be evidenced by the following Fig. 1–5.

Fig. 1 shows the SEM and TEM images of the samples. As can be

shown in Fig. 1a, TiO_2 MS with a diameter of $\sim 3 \mu\text{m}$ are obtained by solvothermal treatment at 150°C for 12 h, and the spheres are composed of nanocrystallites. After being coated with Cu NPs, the surface of microspheres becomes rough (Fig. 1b and d), which is different from the pure TiO_2 MS. It indicates the existence of Cu NPs on the TiO_2 MS. Furthermore, after introducing TCPP onto the Cu NPs coated TiO_2 MS, no scattered particles are observed outside of the microspheres, and the rough surface becomes relatively smooth. Moreover, the sphere-like morphology remains well. It is indicated that TCPP molecules lay on the microspheres. The morphology could be attributed to the unique loading mode of TCPP molecules on the microspheres, which will be further evidenced by Figs. 3–5. Furthermore, the HRTEM of the hybrid shows (111) face of Cu, (020) and (112) faces of CuO on the edge of the microsphere, which indicates that the Cu in the hybrid is mainly in the form of metallic Cu and CuO.

To further clarify the component of the TiO_2 MS-Cu-TCPP, energy-filtered TEM of the hybrid is taken because it can show clearer elemental distribution in the hybrid. Fig. 2 b–f shows the element maps of the hybrid, which are measured according to the image shown in Fig. 2a. It can be seen that there exist Ti, O, Cu, N, C elements in the hybrid, which is consistent with the element composition of the TiO_2 MS-Cu-TCPP. Moreover, the maps of Ti, O, Cu, N, C shown in Fig. 2b–f, respectively, correspond exactly to the TEM image shown in Fig. 2a.

The phase and crystallographic structure of the samples were determined by powder X-ray diffraction (XRD). Fig. 3 shows the XRD patterns of TiO_2 MS, TiO_2 MS-Cu, and TiO_2 MS-Cu-TCPP, respectively. The XRD patterns of all products present similar profiles and major peaks are well coincident with standard JCPDS values (anatase-JCPDS No: 21-1272, rutile-JCPDS No: 21-1276). In addition, a new and weak peak at $2\theta = 42.7^\circ$ is observed at the XRD pattern of the TiO_2 MS-Cu, which can be assigned to the (111) crystal planes of Cu (JCPDS No: 04-0836). It is demonstrated that the Cu^{2+} in the samples has been reduced into metal Cu. The other diffraction peaks of Cu are not found in the Fig. 3, perhaps because of the low content of Cu in the hybrid. In the XRD pattern of the TiO_2 MS-Cu-TCPP, besides the peaks corresponding to TiO_2 , the peak (at $2\theta = 42.7^\circ$) attributed to metal Cu in the TiO_2 MS-Cu is weakened, and a new peak at $2\theta = 47.5^\circ$ is observed, which corresponds to the crystal facet of (112) crystal planes of CuO (JCPDS No: 48-1548). It is deduced that some Cu NPs on the surface of the hybrid could be partially oxidized due to the linking of TCPP on the TiO_2 MS-Cu.

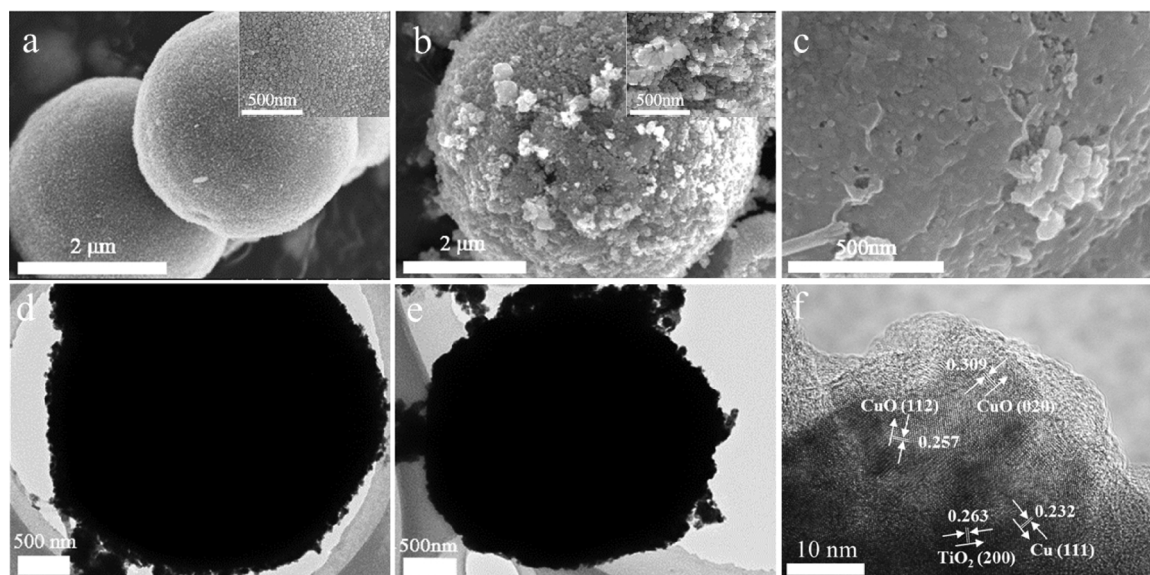


Fig. 1. SEM images of (a) TiO_2 MS, (b) TiO_2 MS-Cu, (c) TiO_2 MS-Cu-TCPP. TEM images of (d) TiO_2 MS-Cu, (e) TiO_2 MS-Cu-TCPP and HRTEM image of (f) TiO_2 MS-Cu-TCPP. The insets were the corresponding enlarged images.

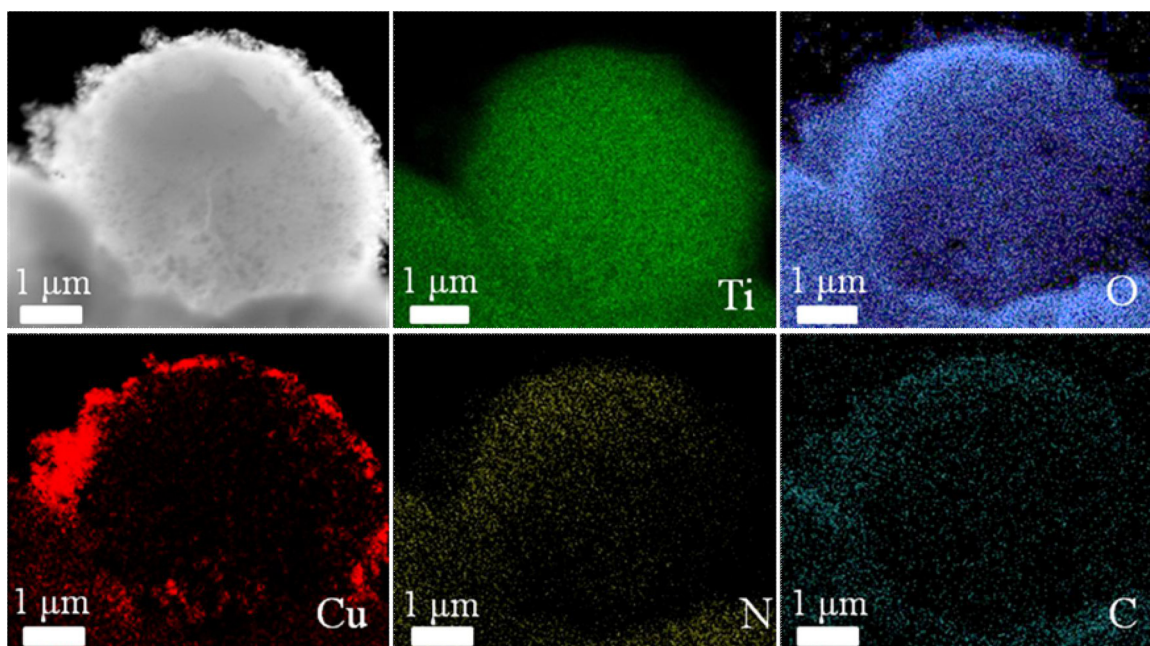


Fig. 2. Energy-filtered TEM images of the TiO_2 MS-Cu-TCPP. (a) TEM image, (b) Ti map; (c) O map; (d) Cu map; (e) N map and (f) C map.

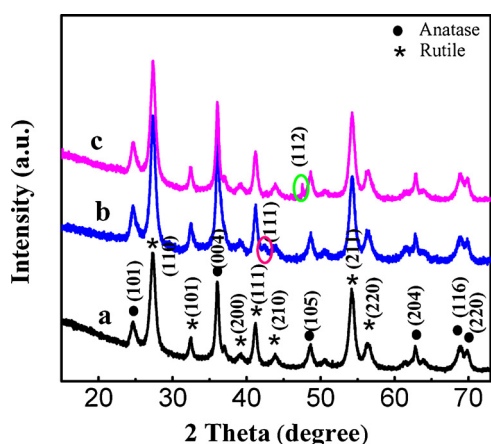


Fig. 3. XRD patterns of (a) TiO_2 MS, (b) TiO_2 MS-Cu and (c) TiO_2 MS-Cu-TCPP.

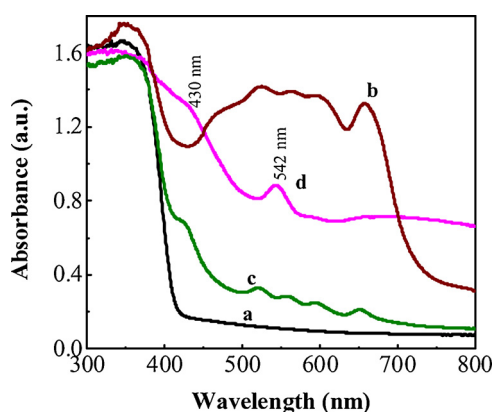


Fig. 4. UV-vis diffuse reflectance absorption spectra of (a) TiO_2 MS, (b) TCPP, (c) TiO_2 MS-TCPP, and (d) TiO_2 MS-Cu-TCPP.

Fig. 4 shows UV-vis diffuse reflectance spectra of the samples, which are recorded in the range of 300–750 nm. Obviously, no absorption is observed above 400 nm for bare TiO_2 MS. The band edge at

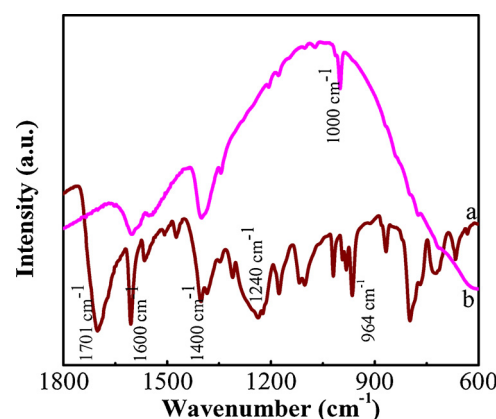


Fig. 5. The FTIR spectra of (a) TCPP and (b) TiO_2 MS-Cu-TCPP.

about 390 nm indicates a band gap of about 3.1 eV, which is consistent with the direct absorption of the intrinsic band gap of TiO_2 [20]. In the spectrum of TiO_2 MS-TCPP (Fig. 4c), the characteristics bands of TCPP can be observed (a Soret band at 423 nm, and four Q bands at 522 nm, 558 nm, 597 nm and 651 nm, respectively). Compared with those of the TCPP, the bands are shifted, which indicate that there exists some interaction between TiO_2 MS and TCPP. Differently, after introducing Cu NPs between TiO_2 MS and TCPP, only one Q band is observed, and the Soret band is red-shifted 7 nm, indicating that TCPP had been linked onto the TiO_2 MS-Cu [21]. According to the spectrum of the TiO_2 MS-Cu-TCPP, it is deduced that TCPP molecules are combined with the TiO_2 MS-Cu in the following two ways: hydrogen bond interaction coming from carboxyl groups of TCPP and hydroxyl groups of TiO_2 MS; and coordination interaction between TCPP macrocycle and the Cu on TiO_2 MS, just like that shown in Scheme 1. The strong interaction between the TiO_2 MS-Cu and the TCPP is very profitable to improving electron transfer and photocatalytic activity of the hybrid, which will be further confirmed by the results in Figs. 5–8.

The binding mode of TCPP and TiO_2 MS-Cu was further confirmed by FTIR (Fig. 5). In Fig. 5, the band at 964 cm^{-1} is assigned to N–H vibration of the pyrrole ring in the TCPP macrocycle. In addition, some functional groups in TCPP, such as, the C=O stretching vibration band

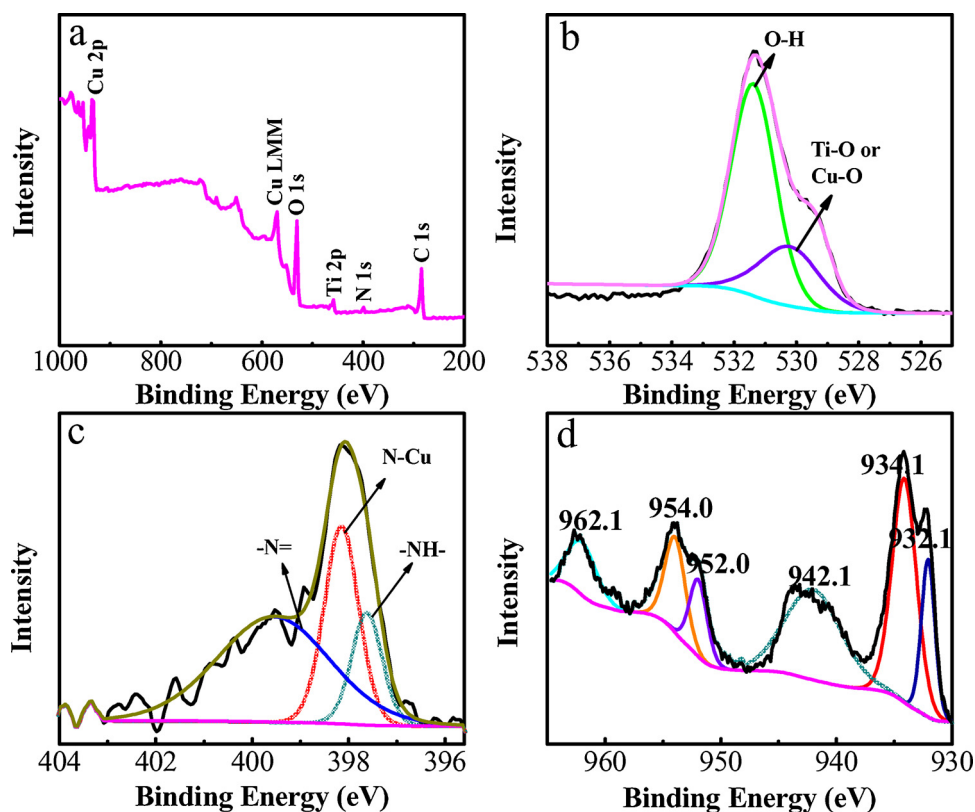


Fig. 6. Typical XPS spectra of the TiO_2 MS-Cu-TCPP: survey spectrum (a), and high resolution XPS spectra of (b) O1s, (c) N1s, and (d) Cu2p.

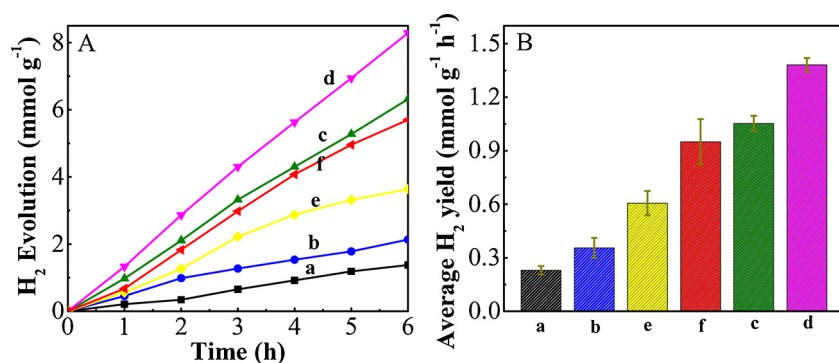


Fig. 7. (A) The dependence of H_2 evolution over various photocatalysts on irradiation time. (B) The H_2 evolution rates over various photocatalysts. TiO_2 MS (a), TiO_2 MS-Cu (b), TiO_2 MS-TCPP (c), TiO_2 MS-Cu-TCPP (d), TiO_2 MS-TCPP-Cu (e) and TiO_2 MS-Cu-TCPP (f).

at 1701 cm^{-1} , the symmetric COO- stretching vibration band at 1600 and 1400 cm^{-1} , and the O-H stretching vibration band at 1240 cm^{-1} [17], can be observed, respectively. After TCPP molecules were linked on the TiO_2 MS-Cu, the bands at 1701 cm^{-1} and 1240 cm^{-1} are almost vanish, supporting the hydrogen bond interaction between TCPP and TiO_2 MS by carboxyl groups of TCPP and hydroxyl groups of TiO_2 MS. In addition, the stretching vibration band at 964 cm^{-1} disappears, and a new band at 1000 cm^{-1} appears. It is one of the most prominent features of the metalation of porphyrin macrocycle [18,22], which indicates that some TCPP molecules coordinate with the Cu on the TiO_2 MS. The results are consistent with those in UV-vis diffuse reflectance absorption spectra (Fig. 4).

More details concerning the elemental compositions and the surface chemical states of the TiO_2 MS-Cu-TCPP nano-micro hybrid were further investigated by X-ray photoelectron spectroscopy (XPS). Fig. 6a shows the representative XPS survey spectrum of the TiO_2 MS-Cu-TCPP hybrid, revealing the existence of Ti, O, Cu, N and C elements within the hybrid, which are consistent with the elemental composition in the

TiO_2 MS-Cu-TCPP hybrid. The high resolution XPS spectra of O1s, N1s and Cu2p are measured and shown in Fig. 6b–d, respectively. In the high resolution XPS spectrum of O1s (Fig. 6b), the peak at the binding energy of ca. 530.3 eV is assigned to Ti-O/Cu-O species, and the one at a higher binding energy of ca. 531.4 eV indicates the presence of hydroxides/ carboxides in the hybrid [23]. In high resolution XPS spectrum of N1s (Fig. 6c), the peaks centered at 399.6 eV and 397.6 eV correspond to =N- and N-H of pyrrole, respectively [18]. The peak centered at 398.1 eV is attributed to Cu-N [24], which indicates the coordination interaction between the Cu and TCPP macrocycle in the hybrid. In the high resolution XPS spectrum of Cu2p (Fig. 6d), two peaks centered at ca. 932.1 and 952.0 eV are attributed to metallic Cu. Because the peaks of Cu are close to those of the Cu_2O [25], Cu_2O is probably present in the hybrid (it was not shown in XRD, also possibly due to its low crystallinity, low content, and good dispersion). The main peaks at ca. 934.1 and 954.0 eV , along with the shakeup satellite peaks at ca. 942.1 and 962.1 eV , indicate the existence of Cu^{2+} [26]. It is deduced that some Cu on the hybrid were oxidized to CuO due to the

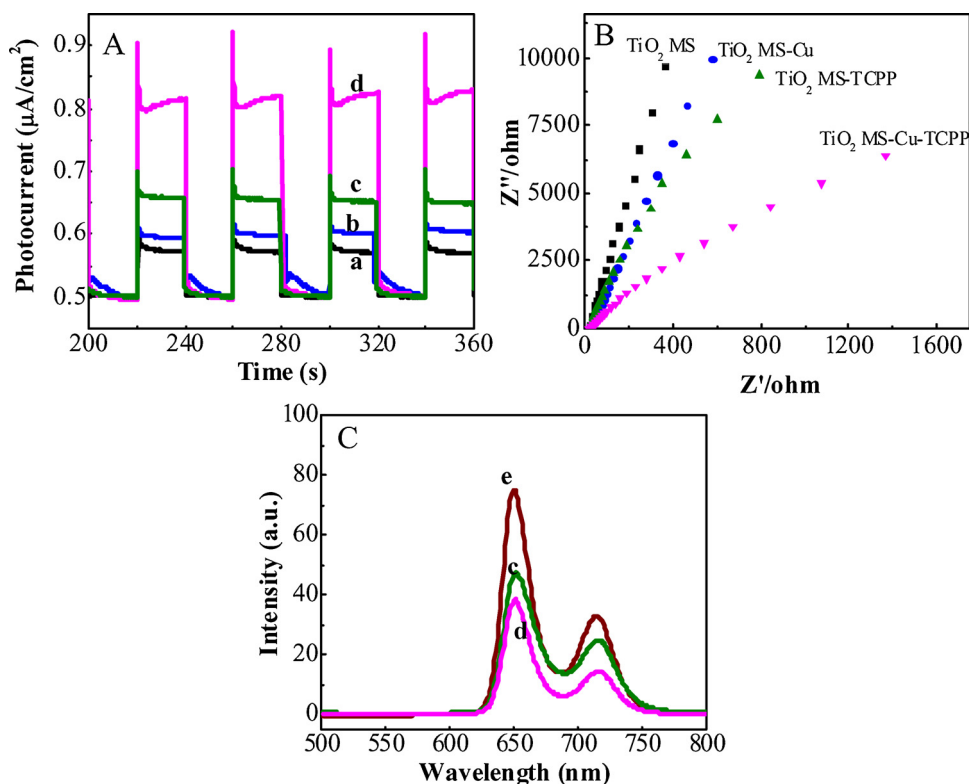


Fig. 8. (A) Transient photocurrents; (B) Nyquist plots of electrochemical impedance spectra and (C) fluorescence spectra of various samples. (a) TiO_2 MS, (b) TiO_2 MS-Cu, (c) TiO_2 MS-TCPP, (d) TiO_2 MS-Cu-TCPP and (e) TCPP. $\lambda_{\text{ex}} = 420 \text{ nm}$.

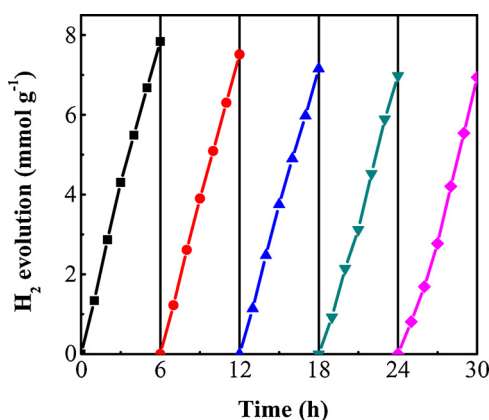


Fig. 9. Cycling measurements of H_2 evolution over the TiO_2 MS-Cu-TCPP nano-micro hybrid.

linking of TCPP on the TiO_2 MS-Cu, which is consistent with the XRD result (Fig. 3c). Subsequently, there exist metallic Cu and $\text{Cu}_2\text{O}/\text{CuO}$ in the TiO_2 MS-Cu-TCPP hybrid. The influence of Cu species on the photocatalytic activity of the hybrid will be further discussed in Figs. 9 and 10.

Based on the results of Fig. 1, Figs. 4–6 and our previous reports [17,18], it is demonstrated that the TiO_2 MS-Cu-TCPP nano-micro hybrid was obtained, and the combination mode of TCPP and TiO_2 MS-Cu can be concluded in two ways: hydrogen bond interaction coming from carboxylic groups of TCPP with the hydroxyl groups on TiO_2 (confirmed by UV-vis spectra and FTIR spectra); and coordination interaction between TCPP macrocycle and the Cu on TiO_2 MS (evidenced by UV-vis spectra, FTIR spectra and XPS spectra), just like that shown in Scheme 1. The intimate contact originated from the dual interaction between TiO_2 MS-Cu and TCPP is very profitable to improving electron transfer and photocatalytic activity of the products. In the absence of any other additives, the assembly of TiO_2 MS-Cu and TCPP may pave a

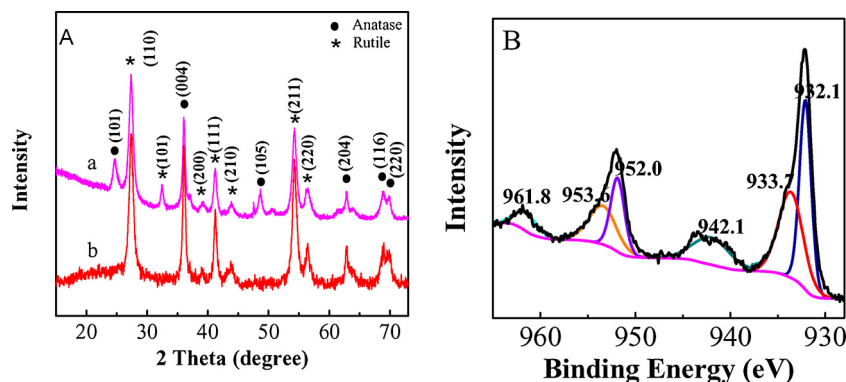


Fig. 10. (A) XRD patterns of the TiO_2 MS-Cu-TCPP: before (a) and after (b) photocatalytic hydrogen evolution. (B) The high resolution XPS spectrum of $\text{Cu}2p$ in the TiO_2 MS-Cu-TCPP after photocatalytic hydrogen evolution.

way for the formation of a novel TiO_2 hybrid by combining hydrogen bond interaction and coordination interaction.

3.2. Photocatalytic activity for hydrogen evolution and electron transfer mechanism

The photocatalytic activity for H_2 production over the as-prepared products was evaluated by using TEOA as sacrificial agents and irradiated under a 300 W xenon lamp. It can be seen that, in Fig. 7, the activity of TiO_2 MS-Cu (Fig. 7b) is higher than that of TiO_2 MS (Fig. 7a), indicating the role of cocatalyst of Cu in the TiO_2 MS. Furthermore, the TiO_2 MS-Cu-TCPP nano-micro hybrid exhibits significantly enhanced photocatalytic activities as compared to those of the TiO_2 MS-TCPP-Cu, TiO_2 MS-Cu-CuTCPP, TiO_2 MS-TCPP, TiO_2 MS-Cu and TiO_2 MS. Its H_2 release rate is enhanced for more than 6 times with respect to the pure TiO_2 MS, resulting from the strong interaction and efficient electron transfer in the hybrid with the Cu as the linker (further evidenced by the followed Fig. 8). Moreover, it is found that the increased amount of hydrogen is different after introducing Cu in the TiO_2 MS and in the TiO_2 MS-TCPP, respectively. It shows larger enhancement when Cu is introduced into TiO_2 MS-TCPP (about 3.8 times higher in TiO_2 MS-Cu-TCPP, and about 2.9 times higher in TiO_2 MS-TCPP-Cu than that introduced in the TiO_2 MS). Moreover, the activity of the TiO_2 MS-Cu-TCPP is 2.3 times higher than that of the TiO_2 MS-TCPP-Cu, and 1.45 times higher than that of the TiO_2 MS-Cu-CuTCPP. Combined with the results in Figs. 3–5, it is demonstrated the important role of Cu in the hybrid as the bridging agent between TiO_2 MS and TCPP, and the synergistic effect of Cu NPs in the TiO_2 MS-Cu-TCPP hybrid, which can facilitate the electron transfer from TCPP to TiO_2 MS. Additionally, the coordination ratio of Cu to TCPP is 1: 1, while the molar ratio of Cu to TCPP in the hybrid is about 1: 0.001. Therefore, only a small amount of Cu covered with TCPP, which is also confirmed by HRTEM of the TiO_2 MS-Cu-TCPP (Fig. 1f, the plane of Cu species can be clearly observed). The rest Cu can act as the cocatalyst, namely, the active sites where H_2 was evolved. Moreover, the photocatalytic activity of the TiO_2 MS-Cu-TCPP (Fig. 7d) is higher than that of the TiO_2 MS-Cu-CuTCPP (Fig. 7f). In addition, visible light absorption of the TiO_2 MS-Cu-CuTCPP and TiO_2 MS-Cu-TCPP is similar. Therefore, the higher activity in the TiO_2 MS-Cu-TCPP is mainly attributed to the coordination of TCPP macrocycle and the Cu species on the TiO_2 MS, and the synergistic effect of Cu NPs in the TiO_2 MS-Cu-TCPP hybrid, which can facilitate the electron transfer from TCPP to TiO_2 MS. These are vital to enhance the photocatalytic activity of a photocatalyst.

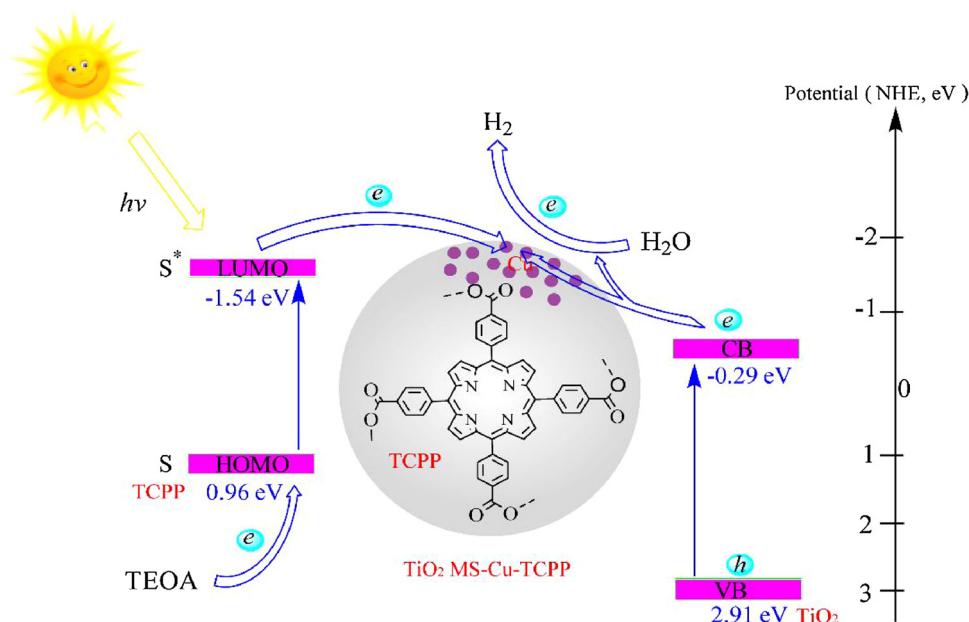
In order to explore the reason for the enhanced photocatalytic activity in the TiO_2 MS-Cu-TCPP nano-micro hybrid, electron transfer, interfacial resistance and fluorescence for the samples are investigated. The separation of photogenerated charge is important for a photocatalyst. To prove the efficient separation of photogenerated charge carriers in the synthesized TiO_2 MS-Cu-TCPP hybrid, photocurrent measurements of the samples were carried out in several on-off intermittent irradiation cycles and the results are shown in Fig. 8A. It reveals that photocurrent intensity enhances when the light is on, and it quickly decreases when the light is off. It is demonstrated that the samples are photosensitive. The photocurrent of all samples is in the order of TiO_2 MS-Cu-TCPP > TiO_2 MS-TCPP > TiO_2 MS-Cu > TiO_2 MS. Obviously, the introduction of TCPP can greatly improve the photocurrent of TiO_2 MS. Furthermore, the TiO_2 MS-Cu-TCPP hybrid shows about 2 times higher photocurrent response than that of the TiO_2 MS-TCPP. The increased photocurrent response for the TiO_2 MS-Cu-TCPP suggests that photogenerated electron-hole pairs are highly separated and recombination rate is decreased under light irradiation. Charge carriers transfer process over the hybrid could be attributed to strong interaction between TCPP and Cu, and also confirms the significant role of Cu in the TiO_2 MS-Cu-TCPP hybrid. Consequently, protons can capture more electrons to form H_2 . Moreover, the photocurrent responses are highly reproducible and remain stable for several on-off cycles,

indicating that the nano-micro hybrid can effectively resist photo-corrosion. In addition, the photocurrent of the TiO_2 MS-Cu is higher than that of the TiO_2 MS, which further supports the dual roles of Cu in the TiO_2 MS-Cu-TCPP hybrid. It is consistent with the results of Fig. 7.

Besides photocurrent response, the charge carrier migration in the TiO_2 MS-Cu-TCPP nano-micro hybrid can be studied by electrochemical impedance spectroscopy. As is shown in Fig. 8B, the diameters of the semicircles at high frequencies for various samples are distinctly different. According to the diameter of the semicircles, the interfacial resistance of the samples is in the order of TiO_2 MS > TiO_2 MS-Cu > TiO_2 MS-TCPP > TiO_2 MS-Cu-TCPP. It is indicated that the introduction of Cu and/or TCPP can efficiently decrease the interfacial resistance of the TiO_2 MS. In addition, electrochemical impedance of the TiO_2 MS-Cu-TCPP hybrid is lower than that of the TiO_2 MS-TCPP. It shows the important role of Cu in the hybrid, which could improve the contact and the interaction between TiO_2 MS and TCPP (Fig. 1c), which is profitable to improving the electron transfer and photocatalytic activity of the TiO_2 MS-Cu-TCPP nano-micro hybrid. The result supports the fact that the introduction of Cu in the TiO_2 MS-TCPP can modify the interaction between TiO_2 MS and TCPP, and has a positive influence on the photocatalytic activity of the TiO_2 MS-TCPP. The result is consistent with that in Fig. 8A.

Furthermore, fluorescence measurements can provide the information on the photogenerated electron-hole separation. The fluorescence spectra of samples are measured and shown in Fig. 8C. Two emission peaks located at 650 nm and 714 nm are observed for the TCPP. After introducing TiO_2 MS and TiO_2 MS-Cu into the TCPP solution, respectively, the fluorescence spectra are similar to that of the TCPP except the quenched emission peaks. It suggests fast photo-induced electron transfer and low charge recombination. Moreover, the weak emission bands indicate that most of the surface states are passivated, making the electrons available for photocatalytic H_2 evolution [27]. Obviously, the recombination of the electrons and holes can be efficiently inhibited, deduced from the decreased fluorescence. It confirms that the interaction between TCPP and TiO_2 MS is strengthened with Cu as the linker. The result is consistent with those in Fig. 8A and B. Therefore, more photogenerated electrons become involved into reducing H^+ to H_2 , which reduces recombination.

Reusability of a photocatalyst is one of the most important factors in catalysis research as well as for practical application. Therefore, recyclability experiments were conducted under a 300 W xenon lamp in order to estimate the stability of the prepared TiO_2 MS-Cu-TCPP nano-micro hybrid. The optimized TiO_2 MS-Cu-TCPP was tested by five consecutive photocatalytic activity experiments, and each reaction was performed for 6 h of irradiation time, as shown in Fig. 9. It can be seen that, there is no obvious loss of photocatalytic activity of hydrogen production after 5 cycles using the TiO_2 MS-Cu-TCPP as the photocatalyst. In the second recycle, the amount of hydrogen evolution over the nano-micro hybrid is slightly decreased, and the amount of hydrogen evolution is hardly changed from the third time. As shown in Fig. 10A, after the illumination, the main peaks corresponding to anatase TiO_2 and rutile TiO_2 are same as those in the as-prepared TiO_2 MS-Cu-TCPP except the peaks corresponding to (101) plane and (105) plane of TiO_2 , which could be caused by the redistribution of Cu and TCPP on TiO_2 MS. In addition, after the illumination, the peaks corresponding to Cu^{2+} decrease, and shift towards low binding energy, which indicate that the Cu^{2+} on the surface of the catalyst can be partially reduced by the H_2 evolved. Referenced to the literature [28], the transformation of Cu^{2+} to the other Cu species (Cu/Cu^+) have positive not negative effect on the activity of TiO_2 MS-Cu-TCPP hybrid. Therefore, the slightly decreased activity in the third time is attributed to the redistribution of Cu and TCPP in the TiO_2 MS, or a certain amount of THPP molecules taken off from the surface of the TiO_2 MS-Cu under the weak basic condition [29] (Measurement of photocatalytic activity was performed in TEOA aqueous solution, and the pH value was about 8–9). Due to the partial loss of the TCPP on the TiO_2 MS-Cu-



Scheme 2. Schematic representation of the electron transfer in the TiO_2 MS-Cu-TCPP nano-micro hybrid under light irradiation.

TCPP, the pH value of the solution is slightly decreased. When the pH value is close to neutral, the TCPP molecules, especially those linked strongly on the TiO_2 MS-Cu-TCPP, are not taken off any more. Therefore, the amount of hydrogen evolution is hardly changed. The result suggests that the photocatalytic activity over the TiO_2 MS-Cu-TCPP hybrid is relatively stable.

In order to explore the enhanced and stable photocatalytic activity over the TiO_2 MS-Cu-TCPP hybrid, a proposed mechanism is schematically illustrated in Scheme 2 (HUMO and LUMO values of TCPP, and CB and VB of TiO_2 were obtained from the references [30,31], respectively). According to the semiconductor photocatalytic theory, the amount of excited electrons in the interface of water and photocatalyst is vital to the photocatalytic activity [32]. In the TiO_2 MS-Cu-TCPP hybrid, excited electrons can be produced by TiO_2 MS and TCPP after irradiation, mainly coming from the TCPP. Since the Fermi level of metal Cu is relatively low comparing to those of TiO_2 and TCPP [33], which is conducive to the photoinduced electrons transfer from TiO_2 MS and TCPP to the Cu. Therefore, the Cu in the TiO_2 MS-Cu-TCPP can act as the transfer passageway of the electrons, which make the recombination of electrons and holes be efficiently avoided. Besides, it can act as the cocatalyst to provide active sites for photocatalytic hydrogen production. Hence, the Cu in the TiO_2 MS-Cu-TCPP hybrid acts as key roles in enhancing the photocatalytic activity of H_2 production. Overall, the constructed TiO_2 MS-Cu-TCPP hybrid photocatalyst can bring the synergistic effect such as enhanced light absorption, improved interfacial charge transfer, and increased reaction centers, which consequently make a significant enhancement on its photocatalytic performance. The photo-produced electrons produced are captured by water molecules, and then the water molecules are reduced into H_2 (Fig. 7), and the holes are consumed by the TEOA.

4. Conclusions

With Cu NPs as the bridging agent, a novel TiO_2 MS-Cu-TCPP nano-micro hybrid was prepared by means of hydrogen bond interaction and coordination interaction. It was found that the Cu had an important influence on the assembly of TCPP on the TiO_2 MS. Moreover, the Cu in the TiO_2 MS-Cu-TCPP can act as the passageway of the electron transfer, which was conducive to the photoinduced electrons transfer and electrons/holes separation. Besides, it can act as the cocatalyst to provide active sites for photocatalytic hydrogen production. Hence, the

constructed TiO_2 MS-Cu-TCPP hybrid photocatalysts can bring synergistic effects such as enhanced light absorption, improved interfacial charge transfer, and increased reaction centers. Subsequently, the hybrid showed about 6 times higher activity than that of the pure TiO_2 MS under the same conditions. It is expected that current work can provide a facile strategy via interface and microstructure modulation for exploring excellent photocatalysts to be used in photocatalytic clean energy production.

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References

- [1] Y. Ma, X.L. Wang, Y.S. Jia, X.B. Chen, H.X. Han, C. Li, Titanium dioxide-based nanomaterials for photocatalytic fuel generations, *Chem. Rev.* 114 (2014) 9987–10043.
- [2] M. Gopannagari, D.P. Kumar, D.A. Reddy, S. Hong, M.I. Song, T.K. Kim, In situ preparation of few-layered WS_2 nanosheets and exfoliation into bilayers on CdS nanorods for ultrafast charge carrier migrations toward enhanced photocatalytic hydrogen production, *J. Catal.* 351 (2017) 153–160.
- [3] Q. Wang, T. Hisatomi, Q.X. Jia, H. Tokudome, M. Zhong, C.Z. Wang, Z.H. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y.B. Li, I.D. Sharp, A. Kudo, T. Yamada, K. Domen, Scalable water splitting on particulate photocatalyst sheets with a solar-to-hydrogen energy conversion efficiency exceeding 1%, *Nat. Mater.* 15 (2016) 611–615.
- [4] H.L. Hou, L. Wang, F.M. Gao, G.D. Wei, J.J. Zheng, B. Tang, W.Y. Yang, Hierarchically porous $\text{TiO}_2/\text{SiO}_2$ fibers with enhanced photocatalytic activity, *RSC Adv.* 4 (2014) 19939–19944.
- [5] M.Z. Ge, C.Y. Cao, J.Y. Huang, S.H. Li, Z. Chen, K.Q. Zhang, S.S.A. Deyabd, Y.K. Lai, A review of one-dimensional TiO_2 nanostructured materials for environmental and energy applications, *J. Mater. Chem. A* 4 (2016) 6772–6801.
- [6] F.Y. Xu, J.J. Zhang, B.C. Zhu, J.G. Yu, J.S. Xu, CuInS_2 sensitized TiO_2 hybrid nanofibers for improved photocatalytic CO_2 reduction, *Appl. Catal. B: Environ.* 230 (2018) 194–202.
- [7] W. Shao, F. Gu, C.Z. Li, M.K. Lu, Interfacial confined formation of mesoporous spherical TiO_2 nanostructures with improved photoelectric conversion efficiency, *Inorg. Chem.* 49 (2010) 5453–5459.
- [8] J.G. Hou, C. Yang, Z. Wang, S.Q. Jiao, H.M. Zhu, Bi_2O_3 quantum dots decorated anatase TiO_2 nanocrystals with exposed {001} facets on graphene sheets for enhanced visible-light photocatalytic performance, *Appl. Catal. B: Environ.* 129 (2013) 333–341.
- [9] M.M. Islam, T. Bredow, Rutile band-gap states induced by doping with manganese

- in various oxidation states, *J. Phys. Chem. C* 119 (2015) 5534–5541.
- [10] S. Meia, J.P. Gao, Y. Zhang, J.B. Yang, Y.L. Wu, X.X. Wang, R.R. Zhao, X.G. Zhai, C.Y. Hao, R.X. Lia, Yan J, Enhanced visible light photocatalytic hydrogen evolution over porphyrin hybridized graphitic carbon nitride, *J. Colloid Interface Sci.* 506 (2017) 58–65.
 - [11] R.Y. Ge, X.Q. Li, S.Z. Kang, L.X. Qin, G.D. Li, Highly efficient graphene oxide/porphyrin photocatalysts for hydrogen evolution and the interfacial electron transfer, *Appl. Catal. B: Environ.* 187 (2016) 67–74.
 - [12] S. Murphy, C. Saurel, A. Morrissey, J. Tobin, M. Oelgemöller, K. Nolan, Photocatalytic activity of a porphyrin/TiO₂ composite in the degradation of pharmaceuticals, *Appl. Catal. B: Environ.* 119 (2012) 156–165.
 - [13] G. Landrou, A.A. Panagiotopoulos, K. Ladomenou, A.G. Coutsolelos, Photochemical hydrogen evolution using Sn-porphyrin as photosensitizer and a series of cobaloximes as catalysts, *J. Porphyrins Phthalocyanines* 20 (2016) 534–541.
 - [14] R. Su, R. Tiruvallam, A.J. Logsdail, Q. He, C.A. Downing, M.T. Jensen, N. Dimitratos, L. Kesavan, P.P. Wells, R. Bechstein, H.H. Jensen, S. Wendt, R.A. Catlow, C.J. Kiely, G.J. Hutchings, F. Besenbacher, Designer titania-supported Au-Pd nanoparticles for efficient photocatalytic hydrogen production, *ACS Nano* 8 (2014) 3490–3497.
 - [15] E.P. Melián, M.N. Suárez, T. Jardiell, J.M.D. Rodríguez, A.C. Caballero, J. Arana, D.G. Calatayud, O.G. Díaz, Influence of nickel in the hydrogen production activity of TiO₂, *Appl. Catal. B: Environ.* 152 (2014) 192–201.
 - [16] M.R. Pai, A.M. Banerjee, S.A. Rawool, A. Singhal, C. Nayak, S.H. Ehrman, A.K. Tripathi, S.R. Bharadwaj, A comprehensive study on sunlight driven photocatalytic hydrogen generation using low cost nanocrystalline Cu-Ti oxides, *Sol. Energy Mater. Sol. Cells* 154 (2016) 104–120.
 - [17] B. Zhuang, X.Q. Li, S.Z. Kang, L.X. Qin, G.D. Li, Assembly and electron transfer mechanisms on visible light responsive 5,10,15,20-meso-tetra(4-carboxyphenyl) porphyrin/cuprous oxide composite for photocatalytic hydrogen production, *Appl. Catal. A* 533 (2017) 81–89.
 - [18] R.Y. Ge, X.Q. Li, B. Zhuang, S.Z. Kang, L.X. Qin, G.D. Li, Assembly mechanism and photoproduced electron transfer for a novel cubic Cu₂O/tetrakis(4-hydroxyphenyl) porphyrin hybrid with visible photocatalytic activity for hydrogen evolution, *Appl. Catal. B: Environ.* 211 (2017) 296–304.
 - [19] L. Tu, H. Pan, H.X. Xie, A. Yu, M.G. Xu, Q.L. Chai, Y.M. Cui, X.F. Zhou, Study on the fabrication and photovoltaic property of TiO₂ mesoporous microspheres, *Solid State Sci.* 14 (2012) 616–621.
 - [20] W.L. Zhen, W.J. Jiao, Y.Q. Wu, H.W. Jing, G.X. Lu, The role of a metallic copper interlayer during visible photocatalytic hydrogen generation over a Cu/Cu₂O/Cu/TiO₂ catalyst, *Catal. Sci. Technol.* 7 (2017) 5028–5037.
 - [21] W. Zhang, C. Wang, X. Liu, J. Li, Enhanced photocatalytic activity in porphyrin-sensitized TiO₂ nanorods, *J. Mater. Res.* 32 (2017) 2773–2780.
 - [22] D.D. La, H.P.N. Thi, Y.S. Kim, A. Rananaware, S.V. Bhosale, Facile fabrication of Cu(II)-porphyrin MOF thin films from tetrakis(4-carboxyphenyl) porphyrin and Cu(OH)₂ nanoneedle array, *Appl. Surf. Sci.* 424 (2017) 145–150.
 - [23] S.S. Lee, H.W. Bai, Z.Y. Liu, D.D. Sun, Novel-structured electrospun TiO₂/CuO composite nanofibers for high efficient photocatalytic cogeneration of clean water and energy from dye wastewater, *Water Res.* 47 (2013) 4059–4073.
 - [24] Y.Y. Liu, Y.M. Yang, Q.L. Sun, Z.Y. Wang, B.B. Huang, Y. Dai, X.Y. Qin, X.Y. Zhang, Chemical adsorption enhanced CO₂ capture and photoreduction over a copper porphyrin based metal organic framework, *ACS Appl. Mater. Interfaces* 5 (2013) 7654–7658.
 - [25] J. Xing, Z.P. Chen, F.Y. Xiao, X.Y. Ma, C.Z. Wen, Z. Li, H.G. Yang, Cu-Cu₂O-TiO₂ nanojunction systems with an unusual electron-hole transportation pathway and enhanced photocatalytic properties, *Chem. Asian J.* 8 (2013) 1265–1270.
 - [26] H.L. Hou, M.H. Shang, F.M. Gao, L. Wang, Q. Liu, J.J. Zheng, Z.B. Yang, W.Y. Yang, Highly efficient photocatalytic hydrogen evolution in ternary hybrid TiO₂/CuO/Cu thoroughly mesoporous nanofibers, *ACS Appl. Mater. Interfaces* 8 (2016) 20128–20137.
 - [27] W.L. Zhen, W.J. Jiao, Y.Q. Wu, H.W. Jing, G.X. Lu, The role of a metallic copper interlayer during visible photocatalytic hydrogen generation over a Cu/Cu₂O/Cu/TiO₂ catalyst, *Catal. Sci. Technol.* 7 (2017) 5028–5037.
 - [28] D.A. Reddy, J. Choi, S. Lee, Y. Kim, S. Hong, D.P. Kumar, T.K. Kim, Hierarchical dandelion-flower-like cobalt-phosphide modified CdS/reduced graphene oxide-MoS₂ nanocomposites as a noble-metal-free catalyst for efficient hydrogen evolution from water, *Catal. Sci. Technol.* 6 (2016) 6197–6206.
 - [29] Y.J. Yuan, J.R. Tu, Z.J. Ye, H.W. Lu, Z.G. Ji, B. Hu, Y.H. Li, D.P. Cao, Z.T. Yu, Z.G. Zou, Visible – light – driven hydrogen production from water in a noble-metal-free system catalyzed by zinc porphyrin sensitized MoS₂/ZnO, *Dyes Pigments* 123 (2015) 285–292.
 - [30] S.K. Mei, J.P. Gao, Y. Zhang, J.B. Yang, Y.L. Wu, X.X. Wang, R.R. Zhao, X.G. Zhai, C.Y. Hao, R.X. Li, J. Yan, Enhanced visible light photocatalytic hydrogen evolution over porphyrin hybridized graphitic carbon nitride, *J. Colloid Interf. Sci.* 506 (2017) 58–65.
 - [31] N.L. Reddy, S. Emin, V.D. Kumari, S.M. Venkatakrishnan, CuO quantum dots decorated TiO₂ nanocomposite photocatalyst for stable hydrogen generation, *Ind. Eng. Chem. Res.* 57 (2018) 568–577.
 - [32] X.B. Chen, S.H. Shen, L.J. Guo, S.S. Mao, Semiconductor-based photocatalytic hydrogen generation, *Chem. Rev.* 110 (2010) 6503–6570.
 - [33] M.A. Mamun, Y. Kusumoto, B. Ahmmad, M.S. Islam, Photocatalytic cancer (HeLa) cell-killing enhanced with Cu-TiO₂ nanocomposite, *Top. Catal.* 53 (2010) 571–577.